

1 474 596

PATENT SPECIFICATION

(11) 1 474 596



BEST AVAILABLE COPY

- (21) Application No. 21274/74 (22) Filed 14 May 1974
- (31) Convention Application No. 48/052 474
- (32) Filed 14 May 1973
- (31) Convention Application No. 48/101 223
- (32) Filed 10 Sept. 1973
- (31) Convention Application No. 48/107 627
- (32) Filed 26 Sept. 1973 in
- (33) Japan (JA)
- (44) Complete Specification published 25 May 1977
- (51) INT CL² C08F 2/00 (C08F 2/00, 2/20, 2/44)
- (52) Index at acceptance
C3P 102 10D1A 10K11 10K4 10K7 10K8 10K9 11D2A1A
11D2A2A 11K10 11K8 11K9 4D3B1 4D3B3 4K10
7D2A1 7K10 8D1A 8D2A 8D2B2 8K10 8K11
8K8 8K9 9D1B1 9K11 9K8 D11 P1C P1E5
P2A1 P2A2 P2A4 P2A5 P2X P4A P4C P4X
P6X PFX T2A

(54) ELECTROSTATIC SPRAY COATING METHOD AND POWDER PAINT COMPOSITION SUITABLE FOR IT

(71) We, TEKKOSHA CO. LIMITED, a Japanese Company, of 4—8, 3-chome, Kyobashi, Chuo-Ku, Tokyo, Japan, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a vinyl electrostatic spray coating powder paint composition and a process for producing it.

Previously, there have been mostly used solution paints in which the paint components are dissolved in organic solvent or emulsion paints in which the paint components have been dispersed in an aqueous medium. However, in the former case environmental pollution is caused by the organic solvents which evaporate while the paint is drying, and in the latter case, the resulting coating lacks certain desirable physical and chemical properties and accordingly, powder paints which do not use a liquid medium have recently appeared, and a painting method using this has been developed, domestic appliances, steel furniture, piping, and automobile parts, for example, having been painted thereby. There are variations in this painting method, but recently particular notice has been taken of an electrostatic dry spray painting method in which powder paint charged to a high voltage has been compelled to flow in air to be deposited electrostatically and to adhere to an article to be painted, whereupon the paint has been melted by heating to form a paint film.

Vinyl powder paint used as the conventional electrostatic dry spray coating powder paint is produced by the following methods:

- (1) After the resin has been dissolved in a solvent and film forming elements such as pigment, plasticizer, and stabilizer, have been added to it, a non-solvent is added with vigorous stirring to precipitate the paint in powder form. 40
 - (2) The resin is melted by heating, pigment and film forming elements are added thereto with stirring, and after cooling the mixture is pulverized by a dissolution pulverizing method. 45
 - (3) The resin pigment and film forming elements are mixed by a high speed rotating mixer in a dry blending method. 50
- However, method (1) must use solvent, and also requires the steps of dissolving resin, depositing powder paint particles and retrieving the solvent. 55
- Since method (2) requires a pulverizing step, the powder particles thus obtained become broken into pieces so that it becomes difficult to form flat and uniform film surfaces. Method (3) can only be used to obtain powder paint coated with pigment particles around the powder particles. 60
- Recently, there have been proposed the following methods in addition to the aforementioned methods. 65
- One of them is a method of producing powder paint containing suspension-polymerizable vinyl chloride monomer or vinyl chloride monomer with another monomer such as vinyl acetate or vinyl ether, in the presence of carbon black by using an oil-soluble polymerization initiator, e.g. an organic peroxide such as diisopropylperoxydicarbonate, or azobisisobutyronitrile (Japanese Patent Publication No. 29475/72). However, in this method, the pigment is not sufficiently dispersed in the powder 70 75

particles. In addition, the size of the powder particles obtained is not constant, the thermostability is poor, and deterioration takes place during storage. Japanese Patent Publication No. 976/73 discloses a method of obtaining a hard vinyl chloride polymer composition adapted for machining which is polymerized by adding agents such as a stabilizer, a lubricating agent, a pigment and a polymer denaturing agent generally contained in hard vinyl chloride polymerization compositions, in advance of or during the polymerizing step, and then adding a polymerization stopping agent to stop the polymerization at a predetermined point.

This method has several disadvantages, for example, the pigment may not be uniformly enclosed in the interior of the polymer particles, the diameters of the particles may not be uniform, and the diameters of the particles may not be optimum, so that the poly-vinyl chloride obtained may be poor in thermal stability.

Japanese Patent Publication No. 10181/73 discloses a method of obtaining a dispersible coating composition in which a resin including a carboxyl group is mixed with pigment, the carboxyl groups in the mixture are neutralised, the mixture emulsified in water, and a polymerizable monomer is added and polymerized. Japanese Patent Publication No. 10182/73 discloses a method of obtained aqueous coating composition in which pigment is mixed with a water-dispersible insoluble resin, the mixture then being emulsified in water by using emulsifying agent or dispersing agent, a polymerizable monomer then being added and polymerized.

However, as a result of this method for producing aqueous compositions the diameters of the particles of polymer are about 1 micron, which is almost the same as the diameters of the particles of the polymer obtained by the conventional emulsion-polymerizing method which are not suitable for electrostatic spray coating.

It is, therefore, an object of the present invention to provide a process for producing a paint composition which is suitable for electrostatic spray coating in which the pigment particles are dispersed substantially uniformly in the paint particles which are of generally spherical shape.

The present invention is based on the following findings:

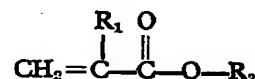
(1) There can be obtained particles mechanically separated between solid and liquid as long as emulsion-polymerization is conducted under vigorous stirring, and there can also be obtained substantially spherical powder particles which have proper size distribution for electrostatic spray coating and which have pigment distributed therein.

(2) If the monomers to be polymerized and pigment and surface active agent and conventional additives such as a deterioration

preventing agent, a fluidity improving agent, an ultraviolet ray absorbing agent, a hardening agent, a thermostability improving agent, if required, are mixed in advance, pigment can be uniformly dispersed in the interior of the particles.

(3) The bulk density of the composition thus obtained is preferably above 0.3 g/cl, and if it is below 0.3 g/cl, when the composition is coated onto a surface and the powder particles thereof are melted to form a coating film, cracks form. Furthermore, in order that this composition may be used as an electrostatic dry spray coating powder paint, the volume intrinsic resistivity of the powder paint particle must be at least 10^9 ohm cm, otherwise the powder particles do not adhere sufficiently to the article to be painted. On the other hand, if the volume intrinsic resistivity of the powder paint particles is above 10^{13} ohm cm, the powder particles tend to become too easily separated from the article to be painted, so that a satisfactory coating film cannot always be obtained. According to one aspect of the invention, we provide a process for preparing a powder composition suitable for dry electrostatic spray coating, comprising the steps of emulsion polymerizing a reaction mixture of:

(i) a first monomer component which is vinyl chloride and/or at least one monomer having the formula:



wherein R_1 is hydrogen or methyl and R_2 is a hydrocarbon group having 1 to 18 carbon atoms, and mixtures of said monomers,

(ii) from 0 to 185 parts by weight, per 100 parts by weight of monomer component (i), of at least one comonomer copolymerizable with monomer component (i) selected from dibutyl maleate, vinyl acetate, vinyl propionate, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, hydroxyethyl acrylate, hydroxyethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, vinyl pyridine, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, dioctyl maleate, styrene, methyl styrene, vinyl toluene, N-methylolacrylamide, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, butadiene, vinyl caprylate, isobutylvinyl ether, vinylidene chloride, itaconic acid, N-phenylmethacrylamide, 2-vinyl naphthalene, allyl acetate, allylacrylate, vinyl isocyanate and vinyl urethane,

(iii) from 0.1 to 50 weight percent, based on the sum of components, (i) and (ii) of a water-insoluble pigment,

(iv) from 3 to 20 weight percent, based on the sum of components, (i) and (ii) of a water-soluble organic surfactant having an HLB value of at least 8,

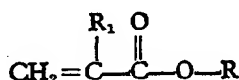
(v) a water-soluble polymerization initiator,

and

(vi) from 200 to 400 weight percent, based on the sum of components (i) and (ii), of an aqueous liquid medium,

5 while simultaneously vigorously agitating the reaction mixture throughout the polymerization such that the circulation number per minute of the reaction mixture is at least 3, wherein the circulation number per minute is equal to the integrated volume of the circulating flow of the reaction mixture per minute divided by the total volume of reaction mixture, in the polymerization vessel to produce substantially spherical polymer particles having a particle size of within the range of 30 to 250 microns, a bulk density of at least 0.3 g/cl and a volume intrinsic resistivity of at least 10^9 ohm-cm; separating the solid polymer particles from the aqueous medium and drying the polymer particles.

20 We also provide a powder paint composition for application to a substrate by a dry electrostatic spray coating process, essentially comprising substantially spherical, polymer particles having a particle size in the range of from 30 to 250 microns, a volume intrinsic resistivity of at least of from 10^9 ohm-cm and a bulk density of at least 0.3 g/cl said polymer particles having pigment particles embedded therein and uniformly dispersed throughout the interior thereof, the surface of the polymer particles being substantially free from adhering pigment particles, said pigment particles present in an amount of from 0.1 to 50 weight percent, based on the sum of the weights of polymer components (i) and (ii), said polymer consisting essentially of units of (i) a first monomer component comprising vinyl chloride and/or at least one monomer having the formula:



wherein R_1 is hydrogen or methyl and R_2 is a hydrocarbon group having 1 to 18 carbon atoms, and mixtures of such monomers, and

45 (ii) from 0 to 185 parts by weight, per 100 parts by weight of monomer component (i), of at least one comonomer copolymerizable with monomer component (i) and selected from dibutyl maleate, vinyl acetate, vinyl propionate, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, hydroxyethyl acrylate, hydroxyethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, vinyl pyridine, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, dioctyl maleate, styrene, methyl styrene, vinyl toluene, N-methylolacrylamide, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, butadiene, vinyl caprylate, isobutyl vinyl ether, vinylidene chloride, itaconic acid, N-phenylmethacrylamide, 2-vinyl naphthalene,

allyl acetate, allyl acrylate, vinyl isocyanate and vinyl urethane.

The monomers represented by the above general formula for the first monomer compound include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexylmethacrylate, lauryl methacrylate, stearyl methacrylate, benzyl acrylate and phenyl acrylate.

Moreover, n-butyl methacrylate and ethyl methacrylate are particularly preferred and when more than two kinds of monomers are used, any mixture in any proportion may be used.

The powder paint composition obtained by the process of the present invention does not undergo blocking during storage because the rate of copolymerisation of the first monomer component with any of the comonomers is faster than the rate of homopolymerisation of the first monomer component.

The ratio of the comonomer to be copolymerised with the first monomer component is normally 0 to 185 parts by weight %, but is preferably 5 to 100 % by weight. If the ratio is less than this latter range, when painting is conducted with the paint composition it is difficult to form a flat and smooth coating film, and if the ratio is more than this latter range, the film obtained is weak.

When the first monomer is vinyl chloride, the mean polymerizing degree of the copolymer is preferably substantially 300 to 600 when measured by JIS (Japanese Industrial Standard) K-6721, and the polymer preferably contains from 0.1 to 1 weight percent of a polyvinyl chloride stabiliser. When the polymerisation degree is less than this range, the endurability and thermostability of the coating film thus obtained are inferior while when it is more than this range, a higher temperature is required when the powder paint is baked after spraying to form the coating film, and accordingly decomposition of plasticizer may be caused.

The pigments used in the present invention include inorganic pigments such as zinc oxide, barium chromate, Prussian Blue, cadmium yellow, antimony sulfide, cadmium red, precipitated barium sulfate, zinc oxide, titanium oxide, red ferric oxide, iron black, chromium oxide, ultramarine blue, precipitated calcium carbonate, carbon black, lamp black, graphite, clay, cobalt blue, and yellow ochre, nitro arylene pigments such as naphthol green B, pigment green B, and naphthol yellow S, azo pigments such as permanent red 4R, brilliant fast scarlet, Hansa (Registered Trade Mark) Yellow 3G, benzidine yellow, linolic red, Lake Red, C, brilliant carmine 6B, permanent red F5R, pigment scarlet 3B, and Para Red, phthalocyanine pigments such as phthalocyanine blue, phthalocyanine green, and Fast

sky blue, and organic pigments such as permanent red BD, isoindoline pigment dioxine violet, aniline black, and quinacridone.

5 The content thereof is 0.1 to 50 percent by weight based on the total amount of monomer used. It is effective for keeping the pigment in the interior of the powder particles and to obtain substantially spherical particles to mix one or more kinds of these pigments with the first monomer component or monomer copolymerizable with the first monomer component, surface active agent, preventing deterioration agent, and/or other additives in advance such as by means of a three-roll mill or ball mill, and then to add them at the beginning of or during polymerization of the remaining monomer(s).

10 In this case, the amount of the monomer used for mixing with the pigment is preferably above 0.5 by weight % based on the monomers. The vinyl paint needs an addition of stabilizer for preventing deterioration, and the agent for preventing deterioration added at the start of polymerization or during polymerization may be, for example, dibutyl tin dilaurate, epoxy soya bean oil, other epoxy compounds such as epoxy resin condensed with epichlorohydrin and 2-2-bis (4-hydroxyphenyl), or 3,4-epoxy-6-methyl-hexylmethyl-3',4'-epoxy-6'-methylcyclohexanecarboxylate. The agent for preventing deterioration can be used in combination with the above mentioned agent. The content thereof is preferably 0.01 to 15% by weight of the total amount of monomer used. Examples of suitable fluidity improving agents are conventional plasticizers such as dibutyl phthalate, 2-ethylhexyl phthalate, 2-ethylhexyl adipate, tricresyl phosphate, tetraisooctyl pyromellitate, chlorides of n-paraffins, high molecular weight polyesters, or epoxy plasticizers.

30 Up to 30 weight percent of a fluidity improving agent can be added, based on the total amount of monomer, and preferably up to 10 percent. The fluidity improving agent may be added all at once at the start of polymerization or gradually during the polymerization.

35 The surface active agents which can be used in the emulsion copolymerization are known surface active agents. They are used in higher proportions than is usual, i.e. at least 3% by weight, preferably at least 5% by weight based on the total monomers. However, it is not economical to use more than 20% by weight. If less than 3% by weight is used, it is difficult to incorporate the pigment into the particles. Suitable surface active agents must have an HLB value (i.e. hydrophilic oleophilic balance) of at least 8, and can include anionic surface active agents as sodium dodecylbenzenesulfonate, polyethyleneglycol alkylethersulfate, or dialkylsulfosuccinic sodium ester, non-ionic surface active agents such as polyethylene glycol sorbitanalkylether, sorbitanalkylester, polyethyleneglycolalkyl-

ether, polyethyleneglycol, or polyethyleneglycolether and cationic surface active agents such as alkylpicolinium chloride, or alkyltrimethylammonium chloride.

70 These surface active agents may be used as mixtures of two or more agents, and thus even when paint is prepared by using two or more pigments together, good results are obtained. In the process of the present invention, the polymerising reaction may be carried out under alkaline or acid conditions, and pH adjusting agents, such as sodium hydrogen carbonate, ammonium carbonate, and acetic acid may be used.

75 Other additives which may be used if required include ultraviolet absorbing agents, thermostability improving agents, molecular weight adjusting agents, fluidity improving agents, and hardening agents. Examples of suitable ultraviolet absorbing agents and thermostability improving agents are 2-hydroxy - 4 - methoxybenzophenone, 2,4-dihydroxybenzophenone, 2 - (2' - hydroxy-5' - methylphenyl)benzotriazole, phenyl salicylate, dioctyl-sulfide, 1,3,8 - triazo - 7,7,9-tetramethyl - 2,4 - dioxy - spiro, 4,5 - tetramethyl - 2,4 - dioxy - spiro, 4,5 - decane, and 2-cyanoethyloctylmercaptan.

80 One or more ultraviolet absorbing agents may be used. Suitable fluidity improving agents include dibutyl phthalate and 2-ethylhexyl phthalate, epoxy resin formed by condensation of epichlorohydrin and 2,2-bis(4-hydroxy-phenyl)propane and resins capable of enhancing the flowability of the coating film. The content thereof is preferably 0.5 to 30% by weight.

85 Suitable molecular weight adjusting agents include mercaptans such as ethylmercaptan, propylmercaptan, butylmercaptan, octylmercaptan, dodecylmercaptan, 2-mercaptoethanol, thiophenol, and ethylmercaptoacetate, and carbon tetrafluoride as a compound effective in chain reactions.

90 A heat curable powder paint of acrylic resin can be produced by this invention.

Suitable heat curing agents for this purpose include dicyandiamide, boron trifluoride-piperidine, and epoxy compound, or acid anhydride which is effective to cure acrylic resins.

95 One or more of these curing agents can be used. They can be added either at the start of polymerisation, gradually during polymerization, or may be added to the emulsion or powder obtained after polymerization has been completed.

100 The vigorous stirring adopted in the present invention is not practised in the prior art methods because it was assumed to produce bad results. In the present invention, this vigorous stirring exerts a particularly good effect on the diameters of the particles of the polymer produced. The size of the polymer particles is closely related to the appearance of the coating film, the performance of the 130

coating film, and ease of electrostatic painting. Thus, in order to obtain a thin coating film, the particles should be small, whereas in order to obtain a thicker coating film, the particles should be large. However, if the particles are too small, the recovery rate of the powder paint during painting becomes poor, so that the results of the painting operation became poorer.

In the process of the present invention, the diameters of the particles may be easily adjusted, and the diameters of the particles are from 30 to 250 microns. Thus, if the grain size of the powder is properly adjusted, it is easy to remove the heat generated during polymerization, and it is also easy to separate the polymerized product.

In order to separate the polymerized product from the reaction mixture, there may be used conventional filtering devices such as centrifugal settling devices and centrifugal filtering devices. For example, decanting type continuous discharge centrifugal settling devices, or basket-type centrifugal filtering devices are particularly preferred.

The drying of the powder particles thus produced may be conducted by conventional methods such as, flash drying methods, fluidised bed drying methods, vacuum drying methods, or drying in a drying oven having shelves, or a combination thereof.

The powder which is in lump form after drying may be adjusted in grain size by using a pulverizer.

According to the present invention, there can be obtained superior vinyl powder paint compositions particularly suitable for electrostatic spray coatings as will be hereinafter described. This improved result is achieved as a consequence of the relatively large amount of the surface active agent as aforementioned, in combination with the vigorous stirring during polymerisation, for example at 200 to 1,200 rpm using a turbine blade-type stirrer with baffle plate, or over 5 revolutions per minute, and preferably 5 to 30 revolutions per minute expressed in terms of mass circulation, i.e. circulating number of times = $\frac{\text{total circulating flow rate}}{\text{total amount of liquid amount to be circulated}}$.

The required conditions for stirring in conventional emulsifying polymerization processes are relatively slow, and the stirring speed of the agitator where a paddle type or anchor type blade stirrer is used is 40 to 60 rpm, or 2 revolutions per minute expressed in terms of mass circulation.

The dispersing medium, polymerization initiating agent and polymerizing degree adjusting agent used in the process of the present invention are all conventional. The dispersing medium may include an aqueous medium such as water, or a water-methanol mixture, and water is preferred. The amount thereof used is 200 to 400% by weight based on the total

monomers. If a smaller proportion of dispersing medium is used it is difficult to remove the polymerizing heat, while if a higher proportion is used, the bulk density of the powder paint composition particles thus obtained is less than 0.30 g/cl, and thus contraction of the coating film occurs during baking so that cracks in the coating are formed. Examples of suitable polymerization initiating agents are hydrogen peroxide, ammonium persulfate, potassium persulfate and water-soluble redox catalysts. Two or more of the above agents may be used in combination. They may be added either at the start of polymerization, or else gradually as the polymerization proceeds. The amount thereof used is preferably 0.01 to 30% by weight based on the total monomers.

As the polymerization adjusting agent, less than 1% by weight of for example carbon tetrachloride, n-butylmercaptan, or thiophenol, based on the total monomer amount may be used. Heretofore, since pigments usually have poor electric insulating properties, the volume intrinsic resistance of powder coatings in which the pigment is dispersed as a coating on the powder particles is normally far broader than the above range. Accordingly, such powders are not satisfactory for use as electrostatic dry spray coating powder paints.

On the other hand, the electrostatic spray coating powder paint composition produced by the present invention does not contain contiguous pigment particles on the surface thereof, but rather the pigment particles are uniformly dispersed in the interior thereof. The powder coating composition produced by this invention also contains an agent for preventing deterioration and, if required, a fluidity improving agent. The composition comprises substantially spherical particles approximately 30 to 250 microns in diameter having a volume intrinsic resistance of at least 10^9 ohm-cm, and a bulk density of at least 0.3 g/cl. Therefore, this powder coating composition exhibits a desirable range of volume intrinsic resistivity so that it is suitable for use as an electrostatic dry spray paint composition, and yet when it is fused by baking after being sprayed onto a product, a satisfactory coating film can be obtained at a lower temperature than is required if a conventional vinyl chloride powder paint is used. This powder paint composition has a bulk density of at least 0.3 g/cl, the particles thereof are substantially spherical in shape, and accordingly no cracking as a result of baking occurs. As the resin components of conventional powder paint, vinyl chloride resins or epoxy resins have mostly been used.

However, epoxy resin powder paint compositions exhibit poor durability, poor anti-shock properties, and poor flexibility. Also they are expensive. Vinyl chloride powder paint compositions do not have these disadvantages and are cheaper, but it has been

difficult until now to provide vinyl chloride paints suitable for electrostatic dry spray painting.

In order to perform the process of the present invention, part or all of the liquid comonomer capable of copolymerising with the first monomer is mixed with part or all of the surface active agent and the pigment, and the powder paint composition is then produced under the conditions described above. This mixing may be easily conducted by conventional methods such as, for example, by using roll mills or ball mills. Thus, the pigment is further dispersed into the particles so that the shapes of the particles are further improved. In this case, the amount of the monomer mixed with the pigment is preferably over 0.5% by weight based on the total monomers used in the polymerization.

Further, if the powder particles containing a thermal decomposition preventing agent on their surface are separated from the aqueous medium after the thermal decomposition preventing agent is added to the reaction system obtained by the emulsion-copolymerization employed in the present invention, there exists a considerable amount of thermal decomposition preventing agent on the surface of the particles which suppresses any decomposition which might otherwise occur upon baking, and accordingly thermal detriment to the other properties of the paint, and therefore, even if a somewhat higher baking temperature is adopted, the coating film does not deteriorate. The process for producing the powder paint has the following advantages:

1) As the powder paint is obtained by the present invention is composed of particles, the exterior surface of which consists of exposed resin, the particles can easily coalesce during fusion. Thus, the baking temperature may be lower by 20 to 40° C compared with powder paints made by conventional dry blending methods.

2) Since the baking temperature can be lower than in the conventional processes, the resin is less subject to deterioration and is thus less discolored.

3) Since spherical particles are obtained in the present invention, the fluidity of the powder itself is superior and the coating film thickness may be easily controlled.

4) The process of the invention is simpler than the conventional methods so that the cost of producing the paint is reduced.

The present invention is further illustrated by the following non-limitative examples.

Unless otherwise indicated, parts in the examples are given on a weight basis.

60

Example 1.

A paste which was prepared by mixing 30 parts of carbon black, 70 parts of polyethylene glycol sorbitan monolaurate, 21 parts

of 3,4 - epoxy - 6 - methylcyclohexyl - 3,4-epoxy - 6 - methylcyclohexanecarboxylate and 95 parts of n-butyl acrylate in a high speed mixer was charged into a reaction vessel having a capacity of 501, and 35 cm in diameter and 78 cm in height provided with an agitator having a turbine vane type impeller 25 cm in diameter, and then 4 parts of ammonium persulfate, 0.5 parts of n-butylmercaptan and 3300 parts of water were introduced into the reaction vessel.

After the reaction vessel had been closed the air in the reaction vessel was replaced by nitrogen gas and further the gas pressure was reduced below atmospheric pressure. Then, 828 parts of vinyl chloride monomer were introduced into the reaction vessel. The agitator was driven at 800 rpm and the reaction mixture was heated to 65° C.

The temperature and the agitation were maintained for 9 hours during which polymerization took place. After the polymerization 50 parts of a polymerized organic mercapto-compound was added as decomposition-preventing agent, followed by agitation for another 30 minutes. The reaction product was recovered by centrifuging the reaction mixture and was then dried.

A polymer powder having an average degree of polymerization of 420, a particle size of 80 to 150 microns, and a bulk density of 0.35 g/cl was obtained with a polymerization yield of 95%. The powder paint thus obtained was applied by electrostatic spray coating to a cold rolled steel plate and the plate bearing the powder paint was heated to 185° C for 5 minutes to fuse the powder.

A beautiful black coating film 100 microns thick was obtained. No blocking of the powder paint was observed when this was stored at 40° C and no trouble arose in storage during the summer. Some physical properties of the powder paint as well as of the coating film formed from it are shown in the Table.

Example 2.

10 parts of a paste which had been prepared by mixing 45 parts of titanium dioxide pigment, 6 parts of carbon black powder, 20 parts of polyethyleneglycol dodecylphenylether, 7 parts of polypropyleneglycol polyethyleneglycolether, 6 parts of tin maleate, 60 parts of ethyl acrylate and 15 parts of lauryl methacrylate in a high speed mixer and further by rolling the resulting mixture in a roller mill having three roller rods were charged into the reaction vessel and used in Example 1 and then 0.2 parts of ammonium persulfate, 0.2 parts of potassium persulfate, 1 part of n-butylmercaptan and 600 parts of water were added into the reaction vessel. After the reaction vessel had been closed the ambient atmosphere in the reaction vessel was replaced by nitrogen gas and further the pressure was reduced below atmospheric pressure. Then 150

parts of vinyl chloride monomer were introduced into the reaction vessel.

The agitator was driven at 600 rpm and the reaction mixture was heated to 70° C. The temperature and the agitation were maintained for 12 hours during the polymerization. After the polymerization 15 parts of di-n-octyl tin-S,S'-bis (isooctyl mercaptoacetate) was added, followed by agitation for another 30 minutes.

The reaction product was recovered by centrifuging the reaction mixture and was then dried. A polymer powder having an average degree of polymerization of 490, a particle size of 50 to 130 microns and bulk density of 0.42 was obtained. The powder paint thus obtained was applied to a cold rolled steel plate by electrostatic spray coating and the plate was then heated to 190° C for 5 minutes to fuse the powder.

A beautiful gray coating film 180 microns thick was obtained. The stability of the powder paint was excellent since no blocking of the powder was observed.

Example 3.

A paste which was prepared by mixing 8 parts of phthalocyanine blue, 18 parts of polyethylene glycol polyether sulfate, 5 parts of di n-butyl maleate, 40 parts of n-butyl acrylate and 10 parts of glycidyl methacrylate in a high speed mixer were charged into a reaction vessel having a capacity of 51, and 15 cm in diameter, 35 cm in height, provided with an agitator having a turbine blade type impeller 25 cm diameter, and then 2 parts of ammonium persulfate and 700 parts of water were added.

After the reaction vessel had been closed, the ambient atmosphere in the reaction vessel was replaced by nitrogen gas and further the pressure was reduced below atmospheric pressure. Then, 150 parts of vinyl chloride monomer were introduced into the reaction vessel.

The agitator was driven at 1,000 rpm and the reaction mixture was heated to 70° C. The temperature and the agitation were maintained for 13 hours during the polymerization. After the polymerization 15 parts of a polymerized organic mercapto-compound was added, followed by agitation for another 30 minutes. The reaction product was recovered by centrifuging the reaction mixture and was then dried. A polymer powder having an average degree of polymerization of 550, particle size of 50 to 160 microns and a bulk density of 0.31 was obtained at a polymerization yield of 95%. This powder paint comprised particles in which the dispersed pigment was substantially covered by the polymer resin. This powder paint could be well coated onto an article of complex shape even at the corner portions when applied by means of electrostatic spray coating. The article was heated to 200° C for 7 minutes to result in a beautiful blue coating 120 microns thick and no appreciable shrinking of the coating film occurred.

It was proved that the stability on storage of the powder paint was excellent and no appreciable blocking phenomenon of the powder was observed at 40° C. Some physical properties of the powder paint as well as those of the coating film formed from it are shown in the Table.

Example 4.

A paste which was prepared by mixing 60 parts of titanium dioxide pigment, 10 parts of sodium dodecylbenzene sulfonate, 22 parts of polyethyleneglycol laurylether, 4 parts of tin maleate and 40 parts of butyl acrylate in a high speed mixer was charged into a reaction vessel having a capacity of 700 l and 16 cm diameter and 326 cm in height provided with an agitator having a turbine vane-type impeller of 40 cm in diameter, and then 1 part of ammonium persulfate, 0.1 parts of thiophenol and 1,500 parts of water were added into the reaction vessel.

After the reaction vessel had been closed the air in the reaction vessel was replaced by nitrogen gas and the pressure was reduced below atmospheric pressure. Then 360 parts of vinyl chloride monomer were introduced into the reaction vessel.

The agitator was driven at 400 rpm and the reaction mixture was heated to 65° C. The temperature and the agitation were maintained for 15 hours during the polymerization. After the polymerization 30 parts of a polymerized organic mercapto-compound was added, followed by agitation for another 30 minutes. The reaction product was recovered by centrifuging the reaction mixture and was then dried. A polymer powder having an average degree of polymerization of 510, particle size of 80 to 150 microns and bulk density of 0.35 was obtained with a polymerization yield of 95%. A beautiful white coating film was obtained by forming a coating using the polymer powder as a powder paint in the similar manner to that described in Example 1 except that a temperature of 190° C was utilized instead of 185° C. It was proved that the stability on storage of the powder paint was excellent and no appreciable blocking phenomenon of the powder was observed, at 40° C.

Example 5.

A paste which was prepared by mixing 10 parts of quinacridone red, 16 parts of alkylpicolinium chloride, 4 parts of epoxidized soybean oil, 0.1 parts of acrylic acid, 30 parts of n-butyl acrylate, 5 parts of methyl methacrylate and 5 parts of diethylhexyl phthalate in a high speed mixer was charged into a reaction vessel having a capacity of 51 and 15 cm diameter and 35 cm in height provided with an agitator having a turbine vane type impeller 8 cm diameter, and then 1 part of ammonium persulfate, 0.04 parts of thiophenol and 450 parts of water were added into the reaction

vessel. After the reaction vessel had been closed the atmosphere in the reaction vessel was replaced by nitrogen gas and the gas pressure was reduced to below atmospheric pressure. Then, 165 parts of vinyl chloride monomer were introduced into the reaction vessel. The agitator was driven at 800 rpm and the reaction mixture was heated to 65° C.

The temperature and the agitation were maintained for 12 hours during the polymerization. After the polymerization 10 parts of a polymerized organic mercapto-compound were added, followed by agitation for another 5 minutes. The reaction product was recovered by centrifuging the reaction mixture and was then dried.

A polymer powder having an average degree of polymerization of 530, a particle size of 50 to 180 microns and a bulk density of 0.45 was obtained at a polymerization yield of 93%.

A beautiful red continuous coating film 80 microns thick was obtained by forming a coating using the polymer powder as the powder paint in a similar manner to that described in Example 4. Since no appreciable blocking phenomenon of the powder paint was observed at 40° C it was proved that the stability on storage thereof was excellent.

Example 6.

A paste which was prepared from 15 parts of Fast yellow pigment, 16 parts of polyethyleneglycol polyether sulfate, 5 parts of tin maleate, 20 parts of methyl acrylate and 3 parts of 2-ethyl-hexyl phthalate in a high speed mixer was charged into the same reaction vessel as was used in Example 3, and then 0.6 parts of potassium persulfate and 500 parts of water were added into the reaction vessel.

After the reaction vessel had been closed the air in the reaction vessel was substituted by nitrogen gas and the gas pressure was reduced below atmospheric pressure. Then, 190 parts of vinyl chloride monomer were introduced into the reaction vessel. The agitator was driven at 1,200 rpm and the reaction mixture was heated to 70° C. The temperature and the agitation were maintained for 8 hours during the polymerization.

After the polymerization 15 parts of a polymerized organic mercapto-compound were added, followed by agitation for another 30 minutes. The reaction product was covered by centrifuging the reaction mixture and was then dried.

A polymer powder having an average degree of polymerization of 560, particle size of 80 to 170 microns and a bulk density of 0.39 was obtained with a polymerization yield of 94%.

A yellow coating 120 microns thick was obtained by forming a coating using the polymer powder as the powder paint in a similar manner to that in Example 1. Since no appreciable blocking phenomenon of the powder paint was observed at 40° C it was proved that the

stability on storage was excellent.

Some physical properties of the powder paints obtained in the above mentioned Examples as well as of the coating film formed by the application listed in the Table, which are compared with the corresponding properties of the powder paints obtained in the below mentioned comparative tests and of the coating films formed therefrom.

Comparative Test 1.

Into the same reaction vessel as was used in Example 3 were charged 0.5 part of polyvinyl alcohol, 0.02 parts of hydroxyethyl cellulose, 0.2 parts of ethylcellulose, 2 parts of ethyl acrylate, 8 parts of vinyl propionate, 0.3 parts of benzoyl peroxide and 400 parts of water. After the reaction vessel had been closed the air in the reaction vessel was substituted with nitrogen gas and further the gas pressure was reduced below atmospheric pressure. Then, 200 parts of vinyl chloride monomer was introduced into the reaction vessel. The agitator was driven at 800 rpm and the reaction mixture was heated to 75° C. The temperature and the agitation were maintained for 8 hours during the polymerization with the result that a polymer powder having an average degree of polymerization of 560 and particle size of 60 to 160 microns was obtained (yield 92%). 100 parts of the thus obtained polymer powder, 40 parts of 2-ethylhexyl phthalate, 15 parts of titanium dioxide pigment and 4 parts of tribasic lead sulfate were mixed in a high speed agitator to a dry-blending process to form a powder paint having particle size of 80 to 190 microns. No practical film was formed by forming a coating from this powder paint in a similar manner to Example 1 except for utilizing a heating temperature of 180° C instead of 185° C. The plate coated with the powder paint was further heated at 210° C for 5 minutes to produce a flat coating 200 microns thick with a vigorous evaporation of the plasticizer content. However the resulting coating film was soft enough to be easily damaged. This test differs from the invention in that the polymerization was carried out in the absence of pigment and surface active agent.

Comparative test 2.

One part of a copolymer of methyl-vinyl-ether and maleic anhydride 0.1 part of hydroxyethylcellulose, 2 parts of ethylcellulose, 42 parts of titanium oxide, 12 parts of epoxy condensation resin with epichlorohydrin and 2,2-bis (4-hydroxyphenyl) propane, 5 parts of benzoyl peroxide, 80 parts of n-butyl acrylate and 533 parts of water were charged into the reaction vessel used in Example 3. After the reaction vessel had been closed the air in the reaction vessel was substituted by nitrogen gas and the gas pressure was reduced below atmospheric pressure. Then 187 parts of vinyl

chloride monomer was introduced into the reaction vessel. The agitator was driven at 1,000 rpm and the reaction mixture was heated to 60° C. The temperature and the agitation were maintained for 15 hours for the polymerization. After the reaction, 20 parts of a polymerized organic mercapto compound were added, followed by agitation for another 30 minutes. The reaction product was recovered by centrifuging the reaction mixture and was dried. White polymer powders having an average degree of polymerization of 490 and particle sizes of 80—300 microns, were obtained with a polymerization yield of 90%, but their surfaces were covered with dispersed pigment, (i.e. resin and pigment separated from one another).

No practical film was formed by forming a coating using this powder paint in a similar manner to that described in Example 1 by heating to 200° C for 5 minutes. The plate covered with the powder paint was further heated at 230° C for 10 minutes to obtain a coating film but the coating film was not flat enough and became discoloured by heat decomposition. This test differed from the invention in that no surface active agent or water soluble polymerization initiator was present during polymerization.

Comparative test 3.

A mixture of the following:

vinyl chloride	280 parts
vinyl acetate	110 parts
n-butyl acrylate	10 parts
titanium oxide	63 parts
polyethyleneglycol sorbitanmonolaurate	19 parts
benzoyl peroxide	11 parts
tin mercapto compound	74 parts
polymerized organic maleate	10 parts
n-butanol	500 parts

was subjected to polymerization under the following polymerization conditions:—

polymerization temperature	65° C
duration of polymerization	40 hours

number of revolutions of agitator 500 rpm

however, the above mentioned polymerized organic mercapto-compound was added after the polymerization reaction was over.

Coarse polymer powders having an average degree of polymerization of 480 and particle size of 500 to 2,000 microns were obtained with a polymerization yield of 87%.

A film was formed by forming a coating using the resulting powder paint at 200° C for 10 minutes but the coating film was weak in heat stability and became discoloured and was rough. The test differed from the invention due to the absence of aqueous medium and a water-soluble polymerization initiator.

Comparative test 4.

A powder paint was produced by using 1/10 part of benzoyl peroxide (oil soluble catalyser) instead of ammonium persulfate and potassium persulfate in Example 2 with the result that there was obtained a powder paint having a particle size of 300 microns in which pigment and resin were separated. It was unsuitable for electrostatic spray coating. This test differed from the invention due to the absence of a water-soluble polymerization initiator.

Comparative test 5.

As in Example 1, polymerization was carried out by using 18 parts of polyethyleneglycol sorbitan monolaurate instead of 70 parts thereof with the result that there was obtained a powder paint having an average degree of polymerization of 400, particle size of 100—200 microns and bulk density of 0.39 at a polymerization yield of 92%, of which the surface was covered with dispersed pigment.

No appreciable film was formed by applying a coating using the resulting powder paint at 220° C.

The powder paint was unsuitable for electrostatic spray coating, for its volume resistivity was remarkably low; i.e. 10⁷Ωcm. This test differed from the invention because less than 3% of surface active agent was used.

Comparative test 6.

In Example 1, the reaction mixture was polymerized by agitation at 150 rpm with the result that the resulting emulsion particles were too small to separate into a solid phase and a liquid phase.

Then 10 parts of sodium chloride were added to the emulsion thereby precipitating the solid component.

The solid component was dried followed by crushing and sizing to obtain a powder paint having a particle size of 40—120 microns. The obtained powder paint was subjected to coating as in Example 1 and the plate bearing the powder paint was heated to 185° C for 9 minutes to fuse the powder.

The coating film was cracked and poor in heat stability. This test differed from the invention in that the agitation was insufficiently vigorous.

Some properties of the powder paint and the coating film are shown in the Table.

Comparative test 7.

A paste which was prepared by mixing 30 parts of titanium white, 18 parts of sorbitanmonostearate (HLB=4.7), 4 parts of tin maleate, 30 parts of n-butyl acrylate and 10 parts of styrene in a high speed mixer was charged into a reaction vessel and 1.0 part of ammonium persulfate, 0.2 parts of n-butylmercaptan and 500 parts of water were added into the reaction vessel.

After the reaction vessel had been closed

the air in the reaction vessel was substituted with nitrogen and the gas pressure was reduced below atmospheric pressure. Then 160 parts of vinyl chloride were introduced into the reaction vessel. The agitator was driven at 800 rpm and the reaction mixture was heated to an elevated temperature and polymerized at the same temperature. There were obtained polymer powders most particles of which were more than 300 micron in diameter and unfit for electrostatic spray coating. This test differed from the invention in that a surface active agent having an HLB of at least 8 was not used.

Example 7.

In the same manner as outlined in Example 1 a paste was prepared from 30 parts of carbon, 90 parts of 2-ethylhexyl phthalate, 70 parts of polyethyleneglycolsorbitan monolaurate, 21 parts of 3,4-epoxy-methylcyclohexanecarboxylate and 9 parts of butyl acrylate.

The paste was charged into the reaction vessel used in Example 1 and then 3 parts of ammonium persulfate and 3300 parts of water were added.

After the reaction vessel had been closed the air in the reaction vessel was substituted by nitrogen gas and the gas pressure was reduced to below atmospheric pressure. Then, 900 parts of vinyl chloride monomer were introduced into the reaction vessel.

The agitator was driven at 800 rpm and the reaction mixture was heated to a temperature of 67° C. The temperature and the agitation were maintained for 9 hours during the polymerization.

After the polymerization, 50 parts of polymerized organic mercapto-compound were added, followed by agitation for another 30 minutes. The reaction product was recovered by centrifuging the reaction mixture and was then dried. A polymer powder having an average degree of polymerization of 500, particle size 70—140 microns and bulk density of 0.38 was obtained at a polymerization yield of 96%.

The powder paint thus obtained was applied to a cooled rolled steel plate by the same procedure as in Example 1. A beautiful black coating film of 100 micron thickness was obtained. No blocking phenomenon of the powder paint was observed at 40° C and no trouble caused by storage during the summer season.

Example 8.

In the same manner as outlined in Example 2, 106 parts of a paste which was prepared from 45 parts of titanium dioxide, 30 parts of 2-ethylhexyl phthalate, 6 parts of carbon black, 25 parts of polyethyleneglycoldodecylphenylether, 7 parts of polypropyleneglycolpolyethyleneglycolether, 6 parts of tin maleate and 2 parts of vinyl acetate were charged into a

reaction vessel as used in Example 2 and then 0.2 parts of ammonium persulfate, 0.2 parts of potassium persulfate, 1 part of n-butylmercaptan and 600 parts of water were added to the reaction vessel. Then, after the procedure outlined in the foregoing examples had been carried out, 230 parts of vinyl chloride monomer were introduced into it.

The agitator was driven at 60 rpm and the reaction mixture was heated to a temperature of 60° C. The temperature and the agitation were maintained for 12 hours for the polymerization.

After the polymerization 15 parts of di-n-octyl-tin-"s s"-bis(isooctyl-mercapto acetate) were added, followed by additional agitation for another 30 minutes. The reaction product was recovered by centrifuging the reaction mixture and this was then dried.

A polymer powder having a polymerization degree of 460, particle size of 40 to 120 micron and bulk density of 0.39 was obtained with a polymerization yield of 93%.

This powder paint was applied to a cold rolled steel plate by means of an electrostatic fluidised bed system and the plate bearing the powder paint was heated to 190° C for 5 minutes.

A beautiful grey coating film 180 microns thick was obtained. The storage stability of the powder paint was excellent since no blocking phenomenon of the powder was observed at a temperature of 40° C.

Example 9.

In the same manner as was outlined in Example 3, a paste prepared from 8 parts of phthalocyanine blue, 16 parts of 2-ethylhexyl adipate, 18 parts of polyethylene glycololeylether sulfate and 5 parts of di n-butylmaleate, was charged into a reaction vessel as was used in Example 3, followed by introducing 2 parts of ammonium persulfate and 700 parts of water.

After the reaction vessel had been closed the air in it was replaced by nitrogen gas and the pressure was reduced below atmospheric pressure.

Then, 200 parts of vinyl chloride were introduced into the reaction vessel, the agitator was driven at 1000rpm and the reaction mixture was heated to 70° C. The temperature and the agitation were maintained for 13 hours during the polymerization.

After the polymerization 15 parts of a polymerized organic mercapto compound were added, followed by agitation for another 30 minutes. The reaction product was recovered by centrifuging the reaction mixture and was then dried. During the drying procedure, there were produced some lumps in the product so that the product was thereafter pulverized by a crusher to pass a sieve of 60 mesh (Tyler Standard Sieve).

A powder polymer having an average degree

of polymerization of 600, particle size of 50 to 200 microns and bulk density of 0.32 was obtained at a polymerization yield of 95%.

The powder paint thus obtained, the paint particles of which were covered with resin, was applied as a coating to a surface of an article of complex shape, with the result that the corners of the article were all coated with a film of the powder paint. The plate bearing the powder paint was heated to 200° C for 7 minutes to fuse the powder.

A beautiful blue coating film of 150 microns thick was obtained. The storage stability of the powder paint was excellent since no blocking phenomena of the powder was observed at 40° C.

Example 10.

There was charged 60 parts of TiO₂ pigment, 20 parts of 2-ethylhexyl phthalate, 20 parts of tricresyl phosphate, 10 parts of sodium dodecylbenzenesulphonate, 22 parts of polyethylene glycol lauryl ether, 4 parts of tin maleate and 3 parts of vinyl propionate into the reaction vessel used in Example 4, and 1 part of ammonium persulfate, 8 parts of carbon tetrachloride and 1,500 parts of water were then added.

After the reaction vessel was closed the air in the reaction vessel was replaced by nitrogen and the pressure was reduced below atmospheric pressure. Then, 400 parts of vinyl chloride monomer were introduced into the reaction vessel.

The agitator was driven at 400 rpm and the reaction mixture was heated to a temperature of 65° C. The temperature and the agitation were maintained for 15 hours during the polymerization. After the polymerization 30 parts of a polymerized organic mercapto-compound was added, followed by agitation for another 30 minutes.

The reaction product was recovered by centrifuging mixture which was then dried.

A polymer powder having an average degree of polymerization of 490, particle size of 70—130 microns and bulk density of 0.34 was obtained at a polymerization yield of 93%.

The powder paint was coated onto a plate by the procedure outlined in Example 7. The plate bearing the powder paint was heated to 190° C for 5 minutes and a beautiful white coating film was obtained. No blocking phenomenon of the powder was observed at even 40° C and the storage stability of the powder was excellent.

Example 11.

There were charged 10 parts of quinacridone red, 35 parts of 2-ethylhexyl phthalate, 16 parts of alkylpicoliniumchloride, 4 parts of epoxysoyabean oil and 0.1 parts of acrylic acid into the reaction vessel used in Example 5, followed by introducing 1 part of ammonium persulfate, 0.1 part of n-butyl mercaptan, 1

part of carbon tetrachloride and 400 parts of water. After following the same procedure as outlined in the foregoing examples, 200 parts of vinyl chloride monomer were introduced. The resulting reaction mixture was heated to 70° C, and stirred at 800 rpm.

The temperature and agitation were maintained for 10 hours during the polymerization.

After the polymerization, 10 parts of a polymerized organic mercapto compound were added, followed by another agitation for 5 hours. The reaction product was recovered by centrifuging the reaction mixture and was dried and passed through a sieve of 60 mesh (Tyler Standard Sieve), accompanied by forcing the residue left on the sieve through the sieve with the fingers.

There was obtained a powder paint having an average degree of polymerization of 480, a particle size of 40 to 200 microns and a bulk density of 0.42 at a polymerization yield of 90%.

The powder paint was coated onto a plate by electrostatic spray coating as outlined in Example 7 and the plate was heated at 190° C for 5 minutes to effect fusion, whereby a beautiful red coating film 150 micron thick was obtained. No blocking phenomenon of the powder paint was observed at 40° C, and the storage stability of the powder paint was excellent.

Example 12.

15 parts of Fast yellow, 16 parts of polyethyleneglycol oleylethersulfate, 5 parts of tin maleate, 1 part of styrene, 10 parts of 2-ethylhexyl phthalate and 10 parts of a high polymer plasticizer; Parablex G—25 (Trade Mark of Rohm and Haas Co.) were mixed well and the resulting mixture was charged into a reaction vessel as used in Example 9, followed by introducing 0.6 parts of potassium persulfate and 500 parts of water. After the reaction vessel was closed the air in the reaction vessel was replaced by nitrogen gas and the pressure was reduced below atmospheric pressure.

Then, 200 parts of vinyl chloride monomer were added and the reaction mixture was heated to 70° C, with stirring at 1,200 rpm.

The agitation and the temperature were maintained for 8 hours during the polymerization. After the polymerization was over, 15 parts of polymerized organic mercapto compound were added, followed by additional agitation for another 30 minutes. The reaction product was recovered by centrifuging the reaction mixture which was then dried.

A polymer powder having an average degree of polymerization of 520, particle size of 50 to 150 microns and bulk density of 0.36 was obtained with a polymerization yield of 95%. The polymer powder was used to coat a plate by the manner described in Example 7, and the plate was heated to 185° C for 5 minutes

to effect fusion, whereby a yellow coating film 100 microns thick was obtained. No blocking phenomenon of the powder was observed at 40° C and the storage stability was excellent.

Some physical properties of the powder paints of Examples 7 to 12 and the coating films formed thereon are given in the Table.

As seen in the Table, the fusing temperatures of the powder paints of these examples were low and the coating films formed from powder paints were excellent in chemical resistance, water resistance and exterior durability.

Comparative test 8.

As in comparative test 2, the reaction mixture was subjected to polymerization using 25 parts of 2-ethylhexyl phthalate instead of 80 parts of butylacrylate and 270 parts of vinyl chloride, instead of 187 parts thereof, at 65° C, thereby obtaining a white powder having an average degree of polymerization of 470 and a particle size of 80—300 microns at a polymerization yield of 90%. The thus obtained powder was covered with pigment particles on its surface, but the pigment and resin were separate from each other. The powder paint was applied to a plate and the plate was heated at 200° C for 5 minutes to fuse the powders, but a practical coating film was not obtained. The plate was further heated to 230° for 10 minutes but although a coating film was obtained, it was rough and became discoloured owing to heat decomposition. In this test, no surface active agent and no water-soluble polymerization initiator was used.

Comparative test 9.

A mixture of the following:

	vinyl chloride	300 parts
40	2-ethylhexyl phthalate	30 parts
	titanium oxide	63 parts
	polyethyleneglycolsorbitanmonolaurate	19 parts
	benzoyl peroxide	11 parts
45	polymerized tin maleate	10 parts
	n-butanol	500 parts

was subjected to polymerization under the following polymerization conditions:

	polymerization temperature	65° C
50	duration of polymerization	40 hours
	speed of stirring	500 rpm

The above mentioned polymerized organic mercapto-compound was added after the polymerization reaction was complete.

A coarse polymer powder having an average degree of polymerization of 460, and particle size of 400 to 800 microns was obtained at a polymerization yield of 85%.

The powder paint was applied to a plate and

then the plate was heated to 200° C for 10 minutes to effect fusion, whereby a practical coating film was obtained, but its storage stability and smoothness were poor. In this test, no aqueous medium or water-soluble polymerization initiator was present.

Comparative test 10.

The same procedure as in Example 8 was followed in manufacturing a powder paint, except for using 1/10 parts of benzoyl peroxide (oil soluble catalyst) instead of ammonium persulfate and potassium persulfate, and a coarse powder paint of about 300 microns in particle size was obtained. This was unsuitable for electrostatic spray coating. In this test, no water-soluble polymerization initiator was present.

Comparative test 11.

The same procedure was followed as in Example 7 in manufacturing a powder paint except for using 18 parts of polyethyleneglycolsorbitanmonolaurate instead of 70 parts thereof. A powder paint having an average degree of polymerization of 480 and particle size of 70 to 150 microns and a bulk density of 0.35 was obtained at a polymerization yield of 90%.

This paint powder was found to be covered continuously with pigment particles on its surface. It was applied to a plate which was then heated to 220° C to effect fusion, but a practical coating film was not obtained. The volume resistivity of the powder had a value as low as 10⁷ ohm cm so that the powder was unsuitable for electrostatic spray coating. In this test, less than 3% (i.e. only about 2%) of surface active agent was used.

Comparative test 12.

The same procedure was followed in polymerizing the reaction mixture as in Example 7, except that the speed of the agitator was 150 rpm.

The solid particles in the resulting emulsion were too small to be separated by centrifuging. Then, 10 parts of sodium chloride was added to the emulsion, thereby precipitating solid component. The precipitate was dried, crushed and sieved, whereby a powder having a particle size of 40 to 120 microns was obtained.

The powder was applied to a plate and the plate bearing the powder was heated to 190° C for 15 minutes to effect fusion. The resulting coating film was worse in thermostability and cracked. In this test, the agitation was insufficiently vigorous.

Comparative test 13.

A paste was prepared by mixing 30 parts of titanium white, 18 parts of sorbitan monostearate (HLB 4.7), 4 parts of tin maleate, 3 parts of butyl acrylate and 20 parts of 2-ethylhexyl phthalate in a high speed mixer. This paste was charged into a reaction vessel,

followed by adding 1 part of ammonium persulfate, 0.2 parts of n-butylmercaptan and 500 parts of water and then the procedure described in the foregoing Examples was carried out. Then, 160 parts of vinyl chloride monomer were added.

The reaction mixture was heated, stirring at 800 rpm, whereby a coarse powder paint, most of the particles of which were larger than 300 microns was obtained. This was unfit for electrostatic spray coating. Some physical properties of the powder paints of the preceding comparative tests 8 to 13 as well as of the coating films formed from them are shown in the Table.

As seen in the Table, the coating films from the comparative test have poor chemical resistance, water resistance and exterior durability and were about 2H hardness of pencil. In this test, a surfactant having an HLB value of at least 8 was not used.

Example 13.

A paste which was prepared by mixing 25 parts of titanium oxide, 6 parts of polyethyleneglycolnonylphenylether of HLB 14, 20 parts of ethyl acrylate and 80 parts of ethyl methacrylate, in a high speed rotating mixer was charged into the reaction vessel used in Example 1, except that the agitator had the same type and number of impellers, of which the arms were 7.5 cm in length, followed by adding 1 part of ammonium persulfate, 0.2 parts of ethylmercaptan and 300 parts of water.

After the air in the reaction vessel had been replaced by nitrogen by the procedure described in the previous Examples, the resulting mixture was heated to 60° C, and stirred at 800 rpm. The temperature and the agitation were maintained for 8 hours during the polymerization. The reaction mixture was treated by the procedure as previously described, so that a powder paint having a particle size of 60 to 130 microns and a bulk density of 0.32 was obtained at a polymerization yield of 95%. The powder paint was applied by electrostatic spray coating to a cold rolled steel sheet (JIS-G-3141) and then the sheet was heated to 200° C for 5 minutes to effect fusion so that a beautiful white coating film 100 microns thick was obtained.

Example 14.

There were mixed 10 parts of carbon black and 20 parts of n-butyl methacrylate and further added 8 parts of sodium dodecylbenzenesulfonate and 180 parts of n-butyl methacrylate using a high speed rotating mixer, to obtain a paste.

The paste was charged into the reaction vessel used in Example 13 followed by adding 0.2 parts of potassium persulfate, 0.3 parts of thiophenol and 500 parts of water.

The resulting mixture was subjected to

polymerization at a temperature of 650° C and stirred at 1,000 rpm over 10 hours whereby a powder paint having a particle size of 60 to 140 microns and a bulk density of 0.35 was obtained at a polymerization yield of 96%.

Pigment particles were dispersed in the interior of the powder paint and the volume intrinsic resistivity thereof was found to be $7 \times 10^{15} \Omega \text{cm}$. The powder paint was used for electrostatic spray coating and baking by the procedure described in Example 13 whereby a beautiful white coating film 50 microns thick was obtained after heating at 180° C for 6 minutes.

Example 15.

To a mixture of 20 parts of titanium oxide, 3 parts of phthalocyanineblue, 120 parts of ethyl methacrylate, and 30 parts of n-butyl methacrylate were added 12 parts of polyethyleneglycolsorbitanmonostearate, and the resulting mixture was mixed using a high speed rotating mixer to obtain a paste. The paste was charged into a vessel as used in Example 1, followed by 0.3 parts of potassium persulfate, 0.3 parts of ammonium persulfate, 0.1 parts of n-butylmercaptan and 400 parts of water.

Then, the air in the reaction vessel was replaced by nitrogen gas. The resulting mixture was subjected to polymerization at a temperature of 70° C and stirred at 700 rpm for 8 hours.

After the reaction was complete, 2 parts of dioctyl sulfide and 1 part of phenyl salicylate were added to the reaction vessel, followed by further stirring for 30 minutes, so that a powder paint having particle sizes of 30 to 120 microns and a bulk density of 0.34 was obtained at a polymerization yield of 93%.

The powder paint did not have a significant quantity of particles on its surface but rather the pigment particles were dispersed in the interior of the particles. The powder paint was applied by electrostatic spray coating to a steel plate by the procedure described in Example 13, and then the plate was heated to 205° C for 5 hours, whereby a beautiful blue coating film 40 microns thick was obtained.

Example 16.

To a mixture of 15 parts of Hansa yellow, 60 parts of ethyl methacrylate, and 40 parts of n-butyl methacrylate, were added 3 parts of dodecylbenzene ethoxysulfate and 4 parts of polyethyleneglycollaurylether. The resulting mixture was mixed in a high speed rotating mixer to obtain a paste. The paste was charged into a reaction vessel as used in Example 1, followed by adding 0.3 parts of ammonium persulfate, 0.05 parts of n-butylmercaptan and 350 parts of water.

After the air in the reaction vessel had been replaced by nitrogen, the reaction mixture was heated to 70° C, with stirring at 700

rpm. The temperature and the agitation were maintained for 6 hours during the polymerization.

5 After the reaction 2 parts of dioctylsulfide were added to the reaction vessel, followed by agitation for 30 minutes. A powder paint having a particle size of 50 to 160 microns and a bulk density of 0.32 was obtained at a polymerization yield of 93%. The powder
10 paint was applied by electrostatic spray coating to a plate as in Example 13, and the plate was heated at 195° C for 6 minutes, whereby a beautiful yellow coating film 80 microns thick was obtained.

15 Example 17.

The procedure of Example 15 was followed, except that after 5 hours from commencement of polymerization, 10 parts of acrylic acid were added to the reaction vessel. After the reaction,
20 Epikote 825 (Registered Trade Mark) was added, followed by agitation for 30 hours. The resulting product was separated from the reaction mixture by a superdecanter and was dried, whereby a powder paint having a particle size of 60 to 120 microns and a bulk
25 density of 0.35 was obtained at a polymerization yield of 94%.

The powder paint, the pigment particles of which were dispersed substantially in the interior thereof was applied by electrostatic
30 spray coating to a plate as used in Example 13 and then the plate was heated to 205° C for 5 minutes, whereby a beautiful pale blue coating film 70 microns thick was obtained.

35 Further heating for 15 minutes more resulted in a hard coating which had good chemical resistance.

Example 18.

40 The procedure of Example 14 was followed, except that after the reaction was over, 10 parts of Epikote 828 (a product of The Shell Chemical Co.) and 11 parts of dicyandiamide were added, followed by agitation for 10 minutes. The resulting product was separated
45 from the reaction mixture by means of a centrifugal separator and was dried, whereby a powder paint having a particle size of 40 to 110 microns and a bulk density of 0.35 was obtained at a polymerization yield of 90%. The powder paint, which substantially contained the pigment in the interior of the particles
50 was applied by electrostatic spray coating to a plate as was used in Example 1 and the plate was heated to 180° C for 5 minutes, whereby a beautiful black coating film was obtained.
55

Example 19.

60 To a mixture of 30 parts of carbon black and 50 parts of methyl methacrylate were added 25 parts of polyethyleneglycolsorbitanmonostearate, 100 parts of methyl methacrylate, 10 parts of methyl acrylate and 3

parts of 4-vinyl pyridine and the mixture was mixed in a high speed rotating mixer to obtain a paste.

65 The paste was charged into a reaction vessel as was used in Example 13, followed by adding 0.1 parts of potassium persulfate, 0.45 parts of sodium bicarbonate and 600 parts of water and then the ambient atmosphere in the reaction
70 vessel was replaced by nitrogen gas. The reaction mixture was heated to 80° C, and stirred at 1,000 rpm. The temperature and the stirring were maintained during the polymerization. After 3 hours from the commencement of the polymerization reaction, there were
75 added 4 parts of glycidyl methacrylate, followed by agitation for 2 hours.

After the polymerization reaction was complete, 2 parts of dioctylsulfide were added, followed by another agitation for 20 minutes, and the resulting emulsion of pH 7.5 was separated using a centrifugal separator.

A powder paint having a particle size of 50 to 150 microns and a bulk density of 0.35 was obtained at a polymerization yield of 95%.

85 The resulting powder paint was applied by electrostatic spray coating to a plate as described in Example 1 and the plate was heated at 200° C for 15 minutes, whereby a beautiful black coating film 90 microns thick was obtained.
90

Example 20.

A mixture of 25 parts of titanium oxide, 5 parts of carbon black, 20 parts of ethyl
95 methacrylate, 80 parts of n-butyl methacrylate, 6 parts of polyethyleneglycolsorbitanmonolaurate, 0.2 parts of ammonium persulfate, 0.2 parts of n-butylmercaptan and 350 parts of water was charged into a reaction vessel as
100 used in Example 13 and then the air in the reaction vessel was replaced by nitrogen.

The reaction mixture was heated at 70° C and stirred at 800 rpm.

105 The temperature and the agitation were maintained for 8 hours during the polymerization.

The reaction product was separated from the reaction mixture by a centrifugal separator and was dried, whereby a powder paint having
110 a particle size of 60 to 150 microns and a bulk density of 0.35 was obtained at a polymerization yield of 98%.

115 The powder paint was applied by electrostatic spray coating to a plate as used in Example 1, and the plate was heated to 205° C for 5 minutes, whereby a grey coating film 100 microns thick was obtained.

120 Some physical properties of the powder paints of each of Examples 13 to 20 as well as of the coating films formed from them are shown in the Table. As can be seen in the Table, the baking temperature of each of these powder paints is low, and each coating film has good chemical resistance and exterior durability.
125

Comparative test 14.

A reaction mixture was subjected to polymerization by the same procedure as in Example 13 except that 3 parts of benzoyl peroxide was used as catalyst.

A powder paint having particle sizes of 50 to 180 microns was obtained at a polymerization yield of 94%.

Since the powder paint particles were not spherical and a portion of the pigment was dispersed on the surface of the particles, the paint was unsuitable for electrostatic spray coating.

The powder paint was applied by electrostatic spray coating to a plate as in Example 13, and the plate was heated to 200° C for 6 minutes, but a coating film was not obtained. The plate was then heated to 200° C for 10 minutes but the resin component decomposed to such a degree that a satisfactory coating film was not obtained. In this test, no water-soluble polymerization initiator was used.

Comparative test 15.

A reaction mixture was subjected to polymerization by the procedure as was followed in Example 14 except that 1,200 parts of water were used. After the reaction, the resulting product was separated from the reaction mixture by means of a centrifugal separator and was then dried, whereby a powder paint having a particle size of 80 to 210 microns and a bulk density of 0.15 was obtained at a polymerization yield of 92%.

The powder paint was applied by electrostatic spray coating to an article of complicated shape and the article was heated to 190° C for 5 minutes whereby a beautiful coating film was obtained except at the corners where the film was cracked. In this test, over 400% (i.e. about 600%) of an aqueous medium was present.

Comparative test 16.

A reaction mixture was subjected to polymerization in a similar manner to that described in Example 14 except that it was stirred at 100 rpm.

After the reaction, the resulting product was treated in a centrifugal separator but most of

the product passed through the filter cloth of the separator and was therefore not recovered.

This proved that there cannot be obtained particles of suitable size for electrostatic spray coating if the emulsion-polymerization is not conducted with vigorous stirring. The powder paint recovered from the surface of the filter cloth was dried. The powder paint was obtained at a polymerization yield of 10% and its particle size was 15 to 45 microns. Then the powder paint was applied by electrostatic spray coating to a plate as in Example 14, and the plate was heated to 180° C for 5 minutes, whereby a coating film 80 microns thick was obtained. In this test, the agitation was not sufficiently vigorous.

Comparative test 17.

A mixture of 80 parts of butyl methacrylate, 20 parts of ethyl methacrylate, 5 parts of polyethylenesorbitanmonostearate, 0.3 parts of potassium persulfate, 500 parts of water and 0.2 parts of n-butylmercaptan was charged into a reaction vessel as used in Example 13.

The reaction mixture was heated to 60° C with stirring at 100 rpm. The temperature and the agitation was maintained for 6 hours during the polymerization, with the result that the resulting polymer could not be separated from the emulsion by a mechanical separator.

Then the emulsion was subjected to salting out, followed by drying and crushing the resulting product. A powder polymer having a particle size of 10 to 25 microns was obtained.

100 parts of the powder polymer, 15 parts of titanium oxide and 10 parts of 2-ethylhexyl phthalate were treated in a high-speed rotating mixer, and a powder paint of particle size 50 to 150 microns was obtained.

The powder paint was applied by electrostatic spray coating to a plate as in Example 13 and the plate was heated to 200° C for 5 minutes, but a coating film was not obtained.

The plate was then heated to 220° C for 10 minutes but the powder paint decomposed to such an extent that a satisfactory coating film was not obtained.

Some physical properties of each powder paint of comparative tests 14 to 17 as well as of each coating film formed by the application thereof are shown in the Table.

TABLE

	Properties of powder paint		Properties of coating film				
	Index of fluidity	Volume resistivity	Baking conditions	Chemicals resistance	Water resistance	Exterior durability	Hardness (pencil test)
Example 1	78	2.5×10^{12} ohm-cm	185 C \times 5 min	⊙	⊙	⊙	2H
Example 2	75	4.2 \times "	190 C \times 5	⊙	⊙	⊙	2H
Example 3	73	2.7 \times "	200 C \times 7	⊙	⊙	⊙	3H
Example 4	70	1.5 \times "	190 C \times 5	⊙	⊙	⊙	2H
Example 5	76	1.8 \times "	190 C \times 5	⊙	⊙	⊙	2H
Example 6	74	2.7 \times "	185 C \times 5	○	○	○	H
Comparative test 1	51.5	0.2 \times "	210 C \times 5	Δ	Δ	×	3B
" 2	53.0	0.2 \times "	200 C \times 5 +210 C \times 10	Δ	Δ	×	H
" 3	—	—	200 C \times 10	Δ	Δ	Δ	HB
" 4	74	2.6 \times "	—	—	—	—	—
" 5	75	1.2×10^7	—	—	—	—	—
" 6	70	3.5×10^{12}	185 C \times 9	×	×	×	2H
" 7	—	—	—	—	—	—	—

TABLE (Continued)

	Properties of powder paint		Properties of coating film				
	Index of fluidity	Volume resistivity	Baking conditions	Chemicals resistance	Water resistance	Exterior durability	Hardness (pencil test)
Example 7	79	1.8×10^{12} ohm-cm	185 C \times 5 min	⊙	⊙	⊙	2H
" 8	73	$2.3 \times "$	190 C \times 5 "	⊙	⊙	⊙	H
" 9	72	$2.8 \times "$	200 C \times 7 "	⊙	⊙	⊙	3H
" 10	74	$1.6 \times "$	190 C \times 5 "	⊙	⊙	⊙	2H
" 11	70	$1.5 \times "$	190 C \times 5 "	○	○	○	HB
" 12	75	$2.2 \times "$	185 C \times 5, "	⊙	⊙	⊙	2H
Comparative test 8	53.0	$0.2 \times "$	200 C \times 5 " +210 C \times 10 "	Δ	Δ	X	2H
" 9	—	—	200 C \times 10 "	Δ	Δ	X	2H
" 10	—	—	—	—	—	—	—
" 11	74	1.5×10^7	—	—	—	—	—
" 12	71	1.7×10^{12}	190 C \times 15 "	X	X	X	2H
" 13	—	—	—	—	—	—	—

TABLE (Continued)

	Index of fluidity	Volume resistivity	Chemicals resistance	Water resistance	Exterior durability	Hardness (pencil test)
Example 13	75	8×10^{14} ohm-cm	⊙	⊙	⊙	3H
" 14	78	7×10^{15} "	⊙	⊙	⊙	2H
" 15	73	5×10^{15} "	⊙	⊙	⊙	3H
" 16	77	2×10^{15} "	⊙	⊙	⊙	3H
" 17	75	2×10^{15} "	⊙	⊙	⊙	4H
" 18	79	6×10^{14} "	⊙	⊙	⊙	4H
" 19	72	6×10^{14} "	⊙	⊙	⊙	4H
" 20	75	4×10^{14} "	⊙	⊙	⊙	3H
Comparative test 14	66	8×10^8 "	X	X	X	3H
" 15	72	8×10^{15} "	○	○	○	2H
" 16	75	3×10^{15} "	⊙	⊙	⊙	2H
" 17	68	4×10^{12} "	-	-	-	-

Note:

1. Index of fluidity was measured by Kah's method using a powder Tester manufactured by Hosokawa Iron Works of Japan. Index of 100 shows best fluidity.
2. Bulk density was measured by method of measuring hardness using the tester as described in Note 1.
3. Volume resistivity was value of resistance when sample was loaded at 500 V, DC for 1 minute using Measurement Instrument of Takeda Riken Co. Ltd.
4. Chemical resistivity was evaluated by discoloration of sample when it was immersed into a 10% NaOH solution and a 10% H₂SO₄ solution respectively for 7 days.
5. Exterior durability was evaluated by the appearance of a sample which had been placed outdoors for one year.
6. Water resistance was evaluated by change of sample which had been immersed in distilled water for one week.
7. Hardness (Pencil Test) was evaluated by attempting to scratch the surface of the coating with sharpened pencils of various hardnesses. The hardness of the film is expressed as the hardness of the softest pencil which can scratch the film when applied to the film at a given pressure. (Japanese Industrial Standard No. JIS K5400).

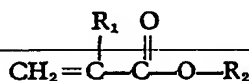
Expressions of evaluation.

- ⊙: splendid ○: good
△: bad ×: very poor

WHAT WE CLAIM IS:—

1. A process for preparing a powder composition suitable for dry electrostatic spray coating, comprising the steps of emulsions polymerizing a reaction mixture of:

- (i) a first monomer component which is vinyl chloride and/or at least one monomer having the formula:



- wherein R₁ is hydrogen or methyl and R₂ is a hydrocarbon group having 1 to 18 carbon atoms, and mixtures of said monomers,

- (ii) from 0 to 185 parts by weight, per 100 parts by weight of monomer component (i), of at least one comonomer copolymerizable with monomer component (i) selected from dibutyl maleate, vinyl acetate, vinyl propionate, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, hydroxy ethyl acrylate, hydroxy ethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, vinyl pyridine, acrylic acid, methacrylic acid, maleic acid, maleic an-

- hydride, dioctyl maleate, styrene, methyl styrene, vinyl toluene, N-methylolacrylamide, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, butadiene, vinyl caprylate, isobutylvinyl ether, vinylidene chloride, itaconic acid, N-phenylmethacrylamide, 2-vinyl naphthalene, allyl acetate, allylacrylate, vinyl isocyanate and vinyl urethane,
- (iii) from 0.1 to 50 weight percent, based on the sum of components, (i) and (ii), of a water-insoluble pigment,
- (iv) from 3 to 20 weight percent, based on the sum of components, (i) and (ii), of a water-soluble organic surfactant having an HLB value of at least 8,
- (v) a water-soluble polymerization initiator, and
- (vi) from 200 to 400 weight percent, based on the sum of components (i) and (ii), of an aqueous liquid medium,

while simultaneously vigorously agitating the reaction mixture throughout the polymerization such that the circulation number per minute of the reaction mixture is at least 3, wherein the circulation number per minute is equal to the integrated volume of the circulating flow of the reaction mixture per minute divided by the total volume of reaction mixture, in the polymerization vessel to produce substantially spherical polymer particles having a particle size of within the range of 30 to 250 microns, a bulk density of at least 0.3 g/cl and a volume intrinsic resistivity of at least 10⁹ ohm-cm; separating the solid polymer particles from the aqueous medium and drying the polymer particles.

2. A process as claimed in Claim 1 in which the circulation number per minute (as herein defined) as a result of vigorous agitation is from 5 to 30.

3. A process as claimed in Claim 1 or 2, in which the reaction mixture contains at least one additive selected from plastic flow improving agents, stabilizers, ultraviolet ray absorbing agents, thermal stability improving agents, molecular weight adjusting agents and curing agents.

4. A process as claimed in any preceding Claim, in which after the emulsion polymerization is completed and before the solid polymer is removed from the aqueous medium, a thermal decomposition preventing agent is added to the reaction system to be absorbed on the surfaces of the polymer particles.

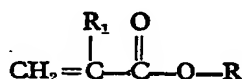
5. A process as claimed in any preceding Claim, in which said monomer component (i) consists essentially of vinyl chloride, the reaction mixture contains from 0.1 to 15 percent by weight, based on the combined weights of components (i) and (ii), of a stabilizer for polymers containing vinyl chloride units, and the degree of polymerization of the polymer is from 300 to 600.

6. A process as claimed in any preceding Claim, in which the said reaction mixture contains a fluidity improving agent.

7. A process as claimed in Claim 1, in which prior to the emulsion polymerization step, the pigment, the surfactant and the monomer component (ii) are premixed to form a uniform paste, and the paste thereby obtained is then mixed with the said aqueous medium and the polymerization initiator and then the chloride is added to and mixed with the reaction mixture and then the reaction mixture is subjected to the emulsion polymerizing step.

8. A process as claimed in Claim 1, in which the reaction mixture contains from 5 to 100 parts of monomer component (ii) per 100 parts by weight of monomer component (i).

9. A powder paint composition for application to a substrate by a dry electrostatic spray coating process, essentially comprising: substantially spherical, polymer particles having a particle size in the range of from 30 to 250 microns, a volume intrinsic resistivity of at least 10^9 ohm-cm and a bulk density of at least 0.3 g/cl, said polymer particles having pigment particles embedded therein and uniformly dispersed throughout the interior thereof, the surface of the polymer particles being substantially free from adhering pigment particles; said pigment particles being present in an amount of from 0.1 to 50 weight percent, based on the sum of the weights of polymer components (i) and (ii), said polymer consisting essentially of units of (i) a first monomer component comprising vinyl chloride and/or at least one monomer having the formula:



wherein R_1 is hydrogen or methyl and R_2 is a hydrocarbon group having 1 to 18 carbon atoms, and mixtures of such monomers, and (ii) from 0 to 185 parts by weight, per 100 parts by weight of monomer component (i), of at least one comonomer copolymerizable with monomer component (i) and selected from dibutyl maleate, vinyl acetate, vinyl propionate, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, hydroxyethyl acrylate, hydroxyethyl methacrylate, diethyl-

aminoethyl acrylate, diethylaminoethyl methacrylate, vinyl pyridine, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, dioctyl maleate, styrene, methyl styrene, vinyl toluene, N-methylolacrylamide, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, butadiene, vinyl caprylate, isobutyl vinyl ether, vinylidene chloride, itaconic acid, N-phenylmethacrylamide, 2-vinyl naphthalene, allyl acetate, allylacrylate, vinyl isocyanate and vinyl urethane.

10. A powder paint composition as claimed in Claim 9, in which said first monomer is vinyl chloride, said polymer containing from 0.1 to 15 percent by weight of a stabilizer for polyvinyl chloride and said polymer having a degree of polymerization of from 300 to 600.

11. A powder paint composition as claimed in Claim 9, in which said polymer consists of monomer units of said formula.

12. A powder paint composition as claimed in Claim 9, in which said polymer contains from 5 to 100 parts by weight of component (ii) per 100 parts by weight of component (i).

13. A powder paint composition as claimed in Claim 9, in which said particles contain one or more additives selected from plastic flow improving agents, stabilizers, ultraviolet ray absorbing agents, thermal stability improving agents, molecular weight adjusting agents and curing agents.

14. A powder paint composition as claimed in Claim 9, in which the surface of said particles have a thermal decomposition preventing agent coated thereon.

15. A process as claimed in Claim 1 in which the vigorous agitation of the reaction mixture is effected by rotating an agitator having turbine blades at from 200 to 1,200 rpm.

16. A powder paint composition as claimed in Claim 13 containing a curing agent selected from dicyanidiamide, boron trifluoride-piperidine, an epoxy compound or an acid anhydride effective to make said polymer thermosetting.

WITHERS & ROGERS,
Chartered Patent Agents,
148-150, Holborn,
London, EC1N 2NT,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.